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TITLE OF INVENTION : Inkjet Recording Paper

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NUMBER OF CLAIMS : 3

REQUEST FOR EXAMINATION : None

Abstract
[Object] To provide an inkjet recording paper that has a quick ink absorbability, smaller spread of ink dots, and good writing property.

[Solution] An inkjet recording paper provided with a coated layer on the substrate paper, where the coated layer contains 10 – 60 weight parts of synthetic amorphous silica prepared by gel method and 40 – 90 weight parts of synthetic amorphous silica prepared by precipitation method. Average particle size of the synthetic amorphous silica prepared by gel method is 2.0 – 10.0 μm, and the average particle size of the synthetic amorphous silica prepared by precipitation method is 3.0 – 8.0 μm. It is desirable that the difference between the average particles of the synthetic amorphous silica prepared by gel method and the synthetic amorphous silica prepared by precipitation method is at least 1.0 μm.

Claims
[Claim 1] Inkjet recording paper provided with a coated layer on a substrate paper, where the coated layer contains 10 – 60 weight part of synthetic amorphous silica prepared by gel method and 40 – 90 weight parts of synthetic amorphous silica prepared by precipitation method.

[Claim 2] The inkjet recording paper according to Claim 1, where the average particle size of synthetic amorphous silica prepared by gel method is 2.0 – 10.0 μm, average particle size of synthetic amorphous silica prepared by precipitation method is 3.0 – 8.0 μm, and the difference of average particles of the synthetic amorphous silica prepared by gel method and the synthetic amorphous silica prepared by precipitation method is at least 1.0 μm.

[Claim 3] The inkjet recording paper according to Claim 1 or Claim 2, where the Becks' flatness/smoothness of the coated layer is 15 – 80 seconds.

Comprehensive explanation of invention
[0001]
[Technological field of invention]
This invention relates to inkjet recording paper, and particularly to inkjet recording paper that has quick ink absorbability, smaller spread of ink dots, and excellent writing property.

[0002]
[Prior art]
Inkjet recording system allows multicolor recording, has relatively high recording speed, and can be used for recording a copy that has a large size. On the other hand, work is underway to improve the ink and equipment to solve the problems of the prior art, such as clogging of nozzle and maintenance problem. Currently, inkjet recording system is widely used in various areas such as in printer, FAX machine, computer terminals and so on, and its field of application is expanding.

[0003]
Now, in color inkjet process, water-based ink solutions having various colors such as cyan (C), magenta (M), yellow (Y), and black (K) are ejected from a plurality of ink nozzles toward the inkjet recording paper. If it is a monochromic flat print made from only one color, the inkjet recording paper needs to absorb only one kind of water-based ink solution of that color. However, in case of a mixed color flat printing using two or more colors such as cyan (C) and green (G) colors and so on, the inkjet recording paper must be able to absorb two or more water-based ink solutions of each colors. Due to this reason, the inkjet recording paper to be used in color inkjet process must have excellent ink absorbability.

[0004]
To improve the ink absorbability, traditionally a paper having a supporting member that can improve the absorbability of a vehicle such as water or solvent by regulating the bulk height, air permeability and degree of sizing, has been proposed. With such conventional paper, the ink droplets tend to spread irregularly on the paper surface, resulting in causing formation of ink streaks that lower the color density. If ink absorbability is deficient, ink seepage may occur due to excessively large spread of the ink dots. And, in a mixed color flat printed area, ink seepage may occur also and thus it has not been possible to obtain a color image that has high density and clearness. On the other hand, even if a paper may excel in ink absorbability, it can not be called a high quality inkjet recording paper if it has deficient surface property and inferior writing property. For inkjet recording paper, excellent surface property and good writing property are important characteristics.

[0005]
[Problems to be solved by the invention]
This invention intends to solve the problems of the prior art and to attain the following objects. Thus, the object of this invention is to provide an inkjet recording paper that has a quick ink absorbability, smaller spread of ink droplets, and good writing property.

[0006]
[Means to solve the problems]
Above-said problems were solved by the following means.

(1) An inkjet recording paper provided with a coated layer on the substrate paper ("substrate", hereinafter), where the coated layer contains 10 – 60 weight parts of synthetic amorphous silica prepared by gel process and 40 – 90 weight parts of synthetic amorphous silica prepared by precipitation process.

(2) The inkjet recording paper described in (1), where the average particle size of the synthetic amorphous silica prepared by gel process is 2.0 – 10.0 μm, the average particle size of the synthetic amorphous silica prepared by precipitation process is 3.0 – 8.0 μm, and the difference between the average particle sizes of the synthetic amorphous silica prepared by gel process and the synthetic amorphous silica prepared by precipitation process is at least 1.0 μm.

(3) The inkjet recording paper described in (1) or (2), where the Becks' flatness/smoothness of the coated layer is 20 – 80 seconds.

[0007]
[Embodiments of invention]
The inkjet recording paper of this invention is formed by providing a coated layer on the substrate. Examples of the substrate are those which are made mainly of wood pulp, such as LBKP or NBPK and so on. If necessary, the substrate may contain synthetic pulp or synthetic fiber and so on. Preferred water drainage after beating is 250 – 450 cc (C.S.F.). The substrate in this invention may contain filler, size, paper reinforcing agent, and fixing agent and so on, as needed.

[0008]
Examples of filler are clay, talc, TiO_2, $CaCO_3$, $BaSO_4$, and so on. Content of filler is normally 0 – 30 weight parts, based on the weight of the pulp. Examples of the size are rosin, alkenyl succinate salts, stearate salts, alkyl ketene dimers, alkenyl succinic anhydride and so on. Examples of the paper reinforcing agent are starch, gelatin, CMC, polyacrylamide and so on. And, examples of the fixing agent are aluminum sulfate, aluminum chloride, polyamide polyamine epichlorohydrin and so on.

[0009]
Density of the substrate is normally 30 – 250 g/m^2, preferably 50 – 150 g/m^2. Thickness of the substrate is normally 30 – 250 μm, preferably 50 – 150 μm. And, preferred whiteness of the substrate (Hunters value) is more than 70%. Preferred rigidity (taper) of the substrate is 1 – 29 g. Preferred water absorbability of the substrate, determined by the procedure specified in JIS P-8140, is 10 – 30 g/m^2. If the water absorbability is less than 10 g/m^2, it tends to create ink streaks. On the other hand, if the water absorbability is more than 30 g/m^2, it tends to form white through-spots.

[0010]
The coated layer contains a synthetic amorphous silica prepared by gel process ("gel process silica", hereinafter) and a synthetic amorphous silica prepared by precipitation method ("precipitation process silica", hereinafter). And, if necessary, the coated layer may contain other components.

[0011]
Gel process is known in the prior art. Thus, sodium silicate and sulfuric acid are mixed instantly to form a hydrosol which is then converted into a hydrogel. After washing the hydrogel with water, it is heated, to control its surface area. Later, this hydrogel is dried and graded, to prepare the synthetic amorphous silica. And, the precipitation process is also known in the prior art. First, sodium silicate and sulfuric acid are mixed. In this case, the silica is precipitated in the solution by controlling the blending condition (temperature, silica concentration, time, etc.). The silica is precipitated and allowed to age. The aged silica is filtered, washed with water, dried, pulverized, and graded, to prepare the synthetic amorphous silica.

[0012]

Specific surface area of the synthetic amorphous silica is 300 – 500 m^2/g, preferably 320 – 450 m^2/g. The specific surface area can be determined by BET adsorption method. If it is smaller than 300 m^2/g, ink absorbability may be poor and the ink may diffuse out. And, if it exceeds 500 m2/g, production of inkjet recording paper may be difficult. Pore volume of the synthetic amorphous silica is greater than 1.0 ml/g, and greater than 1.3 ml/g is preferred. If the pore volume is less than 0.5 ml/g, it may not have sufficient ink absorbability.

[0013]

Average particle size of the gel process silica is 2.0 – 10.0 μm, preferably 3.0 – 10.0 μm. Lower limit of the gel process silica is either the lower limit of the above-described range of average particle size or the average particle size of the gel process silica being adopted in the examples to be described later, and the upper limit of the gel process silica is either the upper limit of the above-described range of average particle size or the average particle size of gel process silica being adopted in the examples to be described later. Incidentally, the average particle size can be determined by using a Coulter counter. If the average particle size of the gel process silica is smaller than 2.0 μm, coating compatibility will be insufficient due to increase of viscosity and production may be difficult. And, if it exceeds 10.0 μm, the surface will have a poor flatness/ smoothness, and spread of the ink dots tend to become larger.

[0014]

Specific surface area of the precipitation process silica is normally 250 – 500 m^2/g, preferably 300 – 400 m^2/g. The specific surface area can be determined by BET adsorption method. If the specific surface area is less than 250 m^2/g, it may show a poor ink absorbability and seepage of ink may occur. If the specific surface area exceeds 500 m^2/g, it will be difficult to prepare the inkjet recording paper. And, as long as the specific surface area is within the preferred range, it is advantageous because the recording paper is free of flaw, has excellent ink absorbability and can prevent effectively the ink seepage. Pore volume of the precipitation process silica is normally greater than 1.0 ml/g, preferably 1.3 ml/g. If the pore volume is smaller than 0.5 ml/g, ink absorbability may often be insufficient.

[0015]

Average particle size of the precipitation process silica is 3.0 – 8.0 μm, preferably 5.0 – 8.0 μm. Lower limit of the average particle size of the precipitation process silica is either the lower limit of the above-described range of average particle size or the average particle size being adopted in the examples to be described later, and the upper limit of the average particle size is either the upper limit of the above-described range of average particle size or the average particle size of precipitation process silica being adopted in the examples to be described later. In this case also, the average particle size can be determined by using a Coulter counter. If the average particle size of the precipitation process silica is smaller than 3.0 μm, coating compatibility will be poor due to increase of viscosity, and production may be difficult. On the other hand, if it exceeds 8.0 μm, the surface will have a poor flatness/smoothness and the ink dots may spread more.

[0016]
In this invention, difference of the average particle sizes of the gel process silica and the precipitation process silica ("particle size difference", hereinafter) is at least 1.0 μm (greater than 1.0 μm), preferably at least 1.5 μm (greater than 1.5 μm). Particle size difference in the range that has the particle size difference being adopted in the examples to be described later as its lower limit, is desirable also. If the particle size difference is smaller than 1.0 μm, writing property may be poor. Such is not the case when the particle size difference is within the above-described preferred range. And, a greater particle size difference tends to give a better writing property, which is an advantage.

[0017]
If total combined amount of the gel process silica and the precipitation process silica in the coated layer is 100 weight parts, the content of the gel process silica in the coated layer is 10 – 60 weight parts, preferably 20 – 40 weight parts, and the content of the precipitation process silica in the coated layer is 40 – 90 weight parts, preferably 60 – 80 weight parts. And, lower limit of the content o gel process silica in the coated layer is either the lower limit of the above-described preferred range or the content of gel process silica being adopted in the examples to be described later. And, the upper limit is either the upper limit of the above-described preferred range or the content of precipitation process silica being adopted in the examples to be described later. And, the lower limit of the content of the precipitation process silica in the coated layer is either the lower limit in the above-described preferred range or the content of precipitation process silica being adopted in the examples to be described later, and the upper limit of the content of precipitation process silica is either the upper limit in the above-described preferred range or the content of precipitation process silica being adopted in the examples to be described later.

[0018]
If the content of gel process silica in the coated layer is less than 10 weight % or if the content of the precipitation process silica exceeds 90 weight %, it will show a poor writing property. And, if the content of the gel process silica in the coated layer exceeds 60% or if the content of precipitation process silica is less than 40 weight %, the ink dots tend to spread excessively, which is not desirable.

[0019]
The gel process silica and the precipitation process silica to be used in this invention may be the ones being prepared in laboratory or may be a commercial product.

[0020]
There is no particular restriction about the other components, and they can be selected appropriately based on the application and object of the inkjet recording paper. Examples are binder, surface active agent, cationic polymers, pigments, light resistance-improving agent, and additives. Among them, it is desirable for the coated layer to contain at least one of the binders.

[0021]

Water-soluble binders and water-dispersible binders can be mentioned as the examples of the binder. Examples of water-soluble binders are starch, catioc starch, casein, gelatin, carboxymethylcellulose, hydroxyethylcellulose, polyvinyl pyrrolidone and so on. Examples of water-dispersible polymers are styrene/butadiene latex, acrylic emulsions and so on. Each of these binders may be used alone, or two or more such binders may be used together.

[0022]

Examples of surface active agent are anionic surface active agents such as carboxylate salts, sulfonate salts, sulfate ester salts, phosphate ester salts and so on; nonionic surface active agent of ether type, ether ester type and so on; amphoteric surface active agents such as betain, aminocarboxylate salts, imidazoline derivatives and so on. Among these surface active agents, sulfonate salts are preferred, and dialkylsulfonate salts such as sodium dimethylpentyl sulfonate and so on are particularly desirable. In case of using dialkylsulfonate salts as the surface active agent, the content is normally 1 – 10 weight parts, preferably 1 – 5 weight parts, per 100 weight parts of the total combined amount of gel process silica and precipitation process silica in the coated layer. If it is less than 1 weight part, ink absorbability tends to be deficient, and more than 10 weight parts tends to lower the color density.

[0023]

Examples of the cationic polymers are cationic resins such as cationic polyacrylamide, cationic polystyrene copolymers, cationic polystyrene copolymers, polydimethyl diallyl ammonium chloride, polyamine polyamide epichlorohydrin (polyamido polyamine epichlorohydrin), polyethylene imine, polyamine sulfone, colloidal silica and so on, which may be used alone or as a mixture of two or more. Among these cationic polymers, cationic polyacrylamide and polyamaine polyamide epichlorohydrin are preferred because of its excellent water resistance.

[0024]

The cationic polyacrylamide is a copolymer of acrylamide and cationic monomer. In some occasions, it may be a ternary copolymer prepared by adding and polymerizing with another monomer component such as (meth)acrylic acid. Examples of the cationic monomer are the compounds represented by the general formula $CH_2=C(R_1)COO-C_nH_{2n}N(R_2)(R_3)$ and the compounds represented by the general formula $CH_2=C(R_1)-CONHC_nH_{2n}N(R_2)(R_3)$ and so on. In these general formula, R_1 represents a hydrogen atom or a lower alkyl group, R_2 and R_3 represent lower alkyl groups, and n represents an integer 1 – 5. Examples of the cationic monomer are dimethylaminoethyl methacrylate $[CH_2=C(CH_3)COOCH_2CH_2N(CH_3)_2]$, diethylaminoethyl methacrylate $[CH_2=C(CH_3)-COOCH_2CH_2N(CH_2CH_3)_2]$, dimethylaminoethyl methacrylate chloride salt $[CH_2=C-(CH_3)COOCH_2CH_2N(CH_3)_2].Cl$, and dimethylaminopropyl acrylamide $[CH_2=CHCONH-CH_2CH_2N(CH_3)_2]$ and so on.

[0025]

Cationic value of the cationic polyacrylamide can be determined in the following manner, for example. Thus, a sample (about 0.1 g) is weighed accurately, and then it is diluted with a solution made of water, methanol and acetic acid (89/10/1, volume %). This solution is titrated with an aqueous N/400 potassium polyvinylsulfate (PVSK) solution, and the cationic value can be calculated by the following formula. Preferred

Cationic value = [Amount used in titration (ml) x 1/400 x factor (PVSK)]/[Amount of sample taken (g) x nonvolatile component (%)/100]

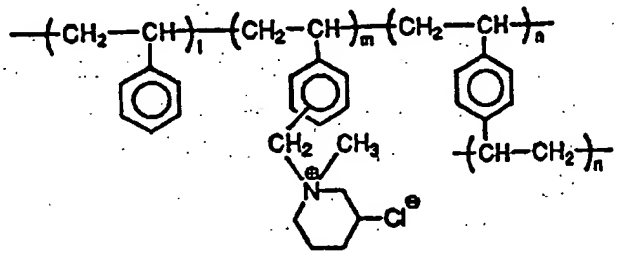
cationic value of the cationic polyacrylamide is 1.5 – 5.0 (meq/g NV). And, preferred molecular weight of the catioinic polyacrylamide is 500,000 – 1,200,000, for example.

[0026]

Compounds having the structure illustrated in Chemical formula 1, for example, can be used as the cationic polystyrene copolymer.

[0027]

[Chemical formula 1]



[0028]

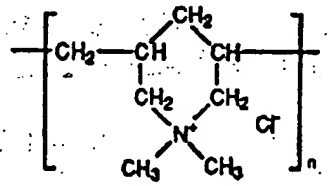
In this structural formula, l, m, and n are, respectively, 1 or more, and preferred l and m are 10 or more, and preferred n is 1 or more. Cationic value of the cationic polystyrene copolymer can be determined in the identical manner like the above-described cationic polyacrylamide, and preferred cationic value is 1.5 – 5 (meq/g NV). And, preferred molecular weight of the cationic polystyrene copolymer is 5,000 – 30,000.

[0029]

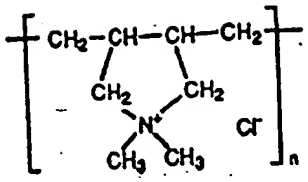
Preferred examples of the polydimethylallyl ammonium chloride are the compounds having a structure represented by Chemical formula 2 and the compounds having a structure represented by Chemical formula 3.

[0030]

[Chemical formula 2]



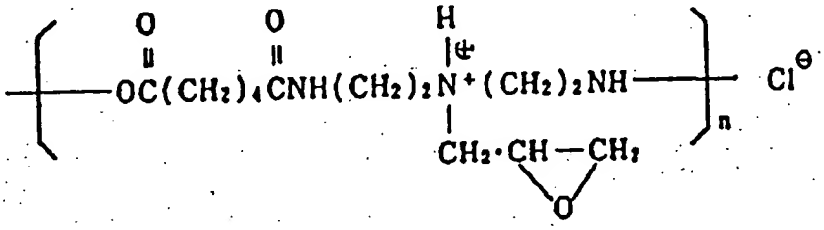
[0031]
[Chemical formula 3]



[0032]
In these structural formula, n represents the degree of polymerization. Cationic value of the polydimethyldiallyl ammonium chloride can be determined like the cationic polyacrylamide, and preferred cationic valaue is 1.5 – 5.0 (meq/g NV). Preferred molecular weight of the polydimethyldiallyl ammonium chloride is 10,000 – 100,000, for example.

[0033]
The polyaminepolyamide epichlorohydrin is also known as an epoxylated polyamide resin, and it is a compound represented by the following structural formula.

[0034]
[Chemical formula 4]



[0035]
The polyaminepolyamide epichlorohydrin can be obtained by adding epichlorohydrin to the secondary amino group of the polyamidepolyamine obtained by dehydrating/ condensing dicarboxylic acid (for example, adipic acid) and a diamine containing a secondary amine in the molecule (for example, diethylenetriamaine), and subsequently acidifying the reaction mixture with hydrochloric acid. Cationic value of the polyamine polyamide epichlorohydrin can be determined like the cationic polyacrylamide, and the preferred cationic value is 1.5 – 5.0 (meq/g NV). Molecular weight of the polyaminepolyamide epichlorohydrin is 20,000 – 150,000, for example.

[0036]
Preferred content of the cationic polymer in the coated layer is 20 – 70 weight parts per 100 weight parts of the total combined weight of the gel process silica and the precipitation process silica.

[0037]
Beside the gel process silica and precipitation process silica, white pigments such as calcium carbonate, kaolin, talc, clay, diatomaceous earth, magnesium silicate, calcium silicate, alumina, zeolite, barium sulfate, urea resin, or melamine resin and so on can be used as the pigment.

[0038]
And, zinc sulfate, zinc oxide, hindered amine type anti-oxidant, benzophenone, and benzotriazole type UV absorber can be mentioned as the examples of light resistance-improving agent. Among them, zinc sulfate is most desirable for this invention.

[0039]
Examples of other additives are pigment dispersing agent, tackifying agent, antifoam, dyes, fluorescent whitener, preservatives, pH regulating agent and so on.

[0040]
The coated layer in this invention is formed by coating a coating solution comprising the gel process silica, precipitation process silica and, if necessary, other components on the substrate and then drying the coated material. The thus-formed coated layer functions as the ink-accepting layer in the inkjet recording paper.

[0041]
There is no particular restriction about the method with which to coat the coating solution on the substrate, and the method can be selected appropriately to match the purpose. For example, curtain coater, roller coater, reverse roll coater, air knife coater, blade coater, spray coater, spin coater and so on can be mentioned. Among them, curtain coater is preferred in this invention because the surface coated with the coating solution, in other words the surface of the coated layer, will have an excellent smoothness and flatness.

[0042]
Amount of the coating solution to be coated on the substrate is normally 6 – 10 g/m^2, preferably 8 – 10 g/m^2 (as solids). If the amount of solids in the coating solution being coated is less than 6 g/m^2, the ink absorbability may be poor. On the other hand, if it exceeds 10 g/m^2, it may cause decrease of color density due to formation of white through-spots. And, if the amount coated is in the above-said preferred range, it shows no flaws, and the inkjet recording paper with excellent ink absorbability, smaller spread of ink dots, and excellent writing property can be prepared.

[0043]
In this invention, the coated layer may be a single layer structure or a laminated structure, depending on the purpose and application of the inkjet recording paper. Incidentally, a coated layer of laminated structure can be formed by coating the coating solution on the substrate and then coating the coating solution again on that coated surface. Smoothness/flatness (as Beck's smoothness/flatness) of the coated layer in the inkjet recording paper of this invention is 15 – 80 seconds, and 20 – 65 seconds

ispreferred. If the Beck's smoothness/flatness is less than 15 seconds, the surface may be rough. And, if it exceeds 80 seconds, it may be have an inferior writing property. Incidentally, Beck's smoothness/flatness can be determined by a commercially available Beck's level meter, for example.

[0044]
In the inkjet recording paper of this invention, a backcoat layer may be formed on the surface opposite to the side where the coated layer is formed. Formation of a backcoat layer on the inkjet recording paper is a definite advantage because it can effectively prevent curling or wrinkling of the inkjet recording paper. The backcoat layer is formed by coating a backcoat layer-forming solution on the surface opposite to the side where the coated layer is formed on the substrate.

[0045]
The backcoat layer-forming solution contains an anionic surface active agent. And, if necessary, it may contain also an antifoam, foam suppresser, dyes, fluorescent whitener, and/or preservative and so on.

[0046]
And, (A) carboxylic acid system, (B) sulfate ester systems, (C) sulfonic acid system, and (D) surface active agents having other hydrophilic groups can be mentioned as the examples of anionic surface active agent. Examples of carboxylic acid system (A) are soaps of aliphatic acids and rosin acids, and salts of ether acids. Examples of sulfate esters are (1) alkyl sulfate ester salts, (2) sulfate esters of aliphatic acid esters and sulfated oils, (3) sulfate ester salts of aliphatic acyl amides, (4) and sulfate ester salts of glycol ethers and so on. Examples of sulfonic acid system (C) are (1) alkylsulfonate salts, (2) dialkyl sulfosuccinate ester salts, (3) alkylallyl sulfonic acid, (4) alkylnaphthalene sulfonate salts, (5) alkyl amide sulfonate salts, and (6) alkyl ester sulfonate salts and so on. And, examples of the surface active agents having other hydrophilic groups are phosphate esters and so on. Among them, dialkyl sulfosuccinate ester salts are preferred, and diethylhexyl sulfosuccinate ester salt is particularly desirable. Of the diethylhexyl sulfosuccinate ester salts, di-2-ethylhexyl sulfosuccinate ester is particularly desirable. And, if di-2-ethylhexyl sulfosuccinate ester is used as the anionic surface active agent, the preferred content in the backcoat layer-forming solution is 0.001 – 0.03 weight %.

[0047]
Surface tension of the backcoat layer-forming solution is normally 25 – 40 dynes/cm. Preferred amount of the backcoat layer-forming solution to be coated is 5 cc/m^2. The backcoat layer-forming solution can be coated by means of a curtain coater, bar coater, gravure coater, roll coater, reverse roll coater, air knife coater, blade coater, spray coater or spin coater and so on.

[0048]
And, if the coated layer has a laminar structure, it is desirable to coat the backcoat layer-forming solution on the surface opposite to the side where the coated layer is to be formed.

[0049]
In case of producing the inkjet recording paper of this invention, after coating the coating solution on one surface of the substrate and then coating the backcoat layer-forming solution on the other surface of the substrate, the coated surfaces are dried. Preferred drying temperature is higher than 80°C because it can prevent curling effectively, and 100°C or higher is particularly desirable. A method using a drum dryer is a preferred drying method, and it is desirable to use a drying method by which the surface coated with the backcoat layer-forming solution contacts with the surface of the drum dryer.

[0050]
An ordinary inkjet printer may be used with the inkjet recording paper of this invention to form a recorded image. However, it is also possible to use a high resolution inkjet printer to form a recorded image.

[0051]
A dye type recording fluid or pigment type recording fluid can be mentioned as the example of recording fluid that can be applied on the inkjet recording paper of this invention. Examples of the dye type recording fluid are the recording fluids containing water-soluble dyes such as direct dyes, acidic dyes, reactive dyes, basic dyes and so on. As the dye type recording fluid, normally the recording fluids having four colors (yellow, magenta, cyan and black) are used. In these colored recording fluids, content(s) of one, two or more water-soluble dye(s) is normally 0.2 – 15 weight parts, preferably 0.5 – 10 weight parts, based on the weight of the total ink composition. And, a content of 2 – 9 weight parts is particularly desirable.

[0052]
Beside water, the recording fluid may also contain a solvent. Examples of the solvent are alkyl alcohols having 1 – 10 carbons such as methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, *sec*-butyl alcohol, *tert*-butyl alcohol, isobutyl alcohol, pentyl alcohol, hexyl alcohol, heptyl alcohol, octyl alcohol, nonyl alcohol, decyl alcohol and so on; aliphatic or aromatic hydrocarbon type solvents such as cyclopentane, hexane, cyclohexane, heptane, octane, nonane, decane, undecane, dodecane, tridecanone, tetralin, decalin, benzene, toluene, and xylene; halogenated hydrocarbon type solvents such as carbon tetrachloride, trichloroethylene, tetrachloroethylene, dichlorobenzene and so on; ether type solvents such as ethyl ether, butyl ether, ethyleneglycol diethyl ether, ethyleneglycol monoethyl ether and so on; ketone type solvents such as acetone, methylethyl ketone, methylpropyl ketone, methylamyl ketone, cyclohexanone and so on; ester type solvents such as ethyl formate, methyl acetate, ethyl acetate, propyl acetate, butyl acetate, phenyl acetate, ethyleneglycol monoethyl ether acetate, ethyl lactate and so on; polyvalent alcohols such as ethyleneglycol, diethyleneglycol, propyleneglycol, glycerin and so on; amines; amides; nitrogen heterocyclics such as N-methyl-2-pyrrolidone, 1,3-dimethyl-2-imidazolidinone and so on; intramolecular oxycarboxylate ester type solvents such as valerolactone, caprolactone and so on; aliphatic sulfone compound type solvents such as dimethyl sulfone, diethyl sulfone, BIS(2-chloroethyl) sulfone, methyl sulfonyl acetonitrile and so on; alicyclic sulfone compound type solvents

such as sulforane, sulforene and so on; and sulfoxide compound type solvents such as tetramethylene sulfoxide, 3-methyltetramethylene sulfoxide and so on.

[0053]
Recording fluid prepared by dispersing the fine pigment particles in an aqueous dispersion medium containing a polymer having hydrophilic constituent and hydrophobic constituent and also an water-soluble organic solvent is preferred as the pigment type recording fluid. Examples of the polymer are polyacrylic acid, polymethacrylic acid, condensed naphthalene sulfonic acid, and styrene/maleic acid copolymer that have a molecular weight of 1,000 – 100,000 or thereabout. These polymers can be made soluble or dispersible in the aqueous liquid by forming a salt. Examples of the components that can form polymer salts are alkaline metals, aliphatic amines, alcohol amines, morpholine, N-morpholine and so on. Examples of the water-soluble organic solvent are alcohols. And, in this invention, polyvalent alcohols are particularly suitable.

[0054]
A recording fluid having a viscosity in a certain range can be obtained by mixing and dispersing the polymer, aqueous organic solvent, water and fine pigment particles. Examples of the fine pigment particles to be used in this recording fluid are various known types of organic pigments such as azo type, phthalocyanine, quinacridone, anthraquinone, dioxazine, indigos, perynone type and so on.

[0055]
This invention is explained further by the following examples which, however, are not intended to limit the scope of this invention.

[0056]
Example 1
< Preparation of substrate >
Wood pulp made of LBKP 80 weight parts and NBKP 20 weight parts was beaten in a disk finery, to obtain a pulp slurry having Canadian Freeness = 400 ml. While the thus-obtained pulp slurry was being agitated, talc 5 weight parts, rosin 1.2 weight part, starch 1.5 weight part, and aluminum sulfate 1.5 weight part were added to pulp 100 weight parts, and this mixture was processed in a long net paper making machine, to form a paper stock having a density of 80 g/m^2. During the course of making a paper, oxidized starch (1.0 g solid/m^2) was attached on the surface of the paper by means of a surface size press, to form a coating substrate. Thickness of the substrate was 95 μm, and Cobbs (SIC) water absorbability was 21.0 g/m^2.

[0057]
< Preparation of coating solution and formation of coated layer >

Gel process silica (specific surface = 360 m^2/g, average particle size = 8.0 μm)	35 weight parts
Precipitation process silica (specific surface = 360 m^2, average particle size = 6.0 μm)	65 weight parts

Silanol-modified polyvinyl alcohol	45 weight parts
Polyamine polyamide epichlorohydrin	35 weight parts
Sodium dimethylpentyl sulfonate	2 weight parts

Water was added to the above composition, to prepare a coating solution having 20 weight % solids. This coating solution was coated on the substrate by means of a curtain coater (amount coated = 8 g solid/m^2). After drying, it was calendered , to form an inkjet recording paper. Incidentally, the average particle size was measured by using a commercial Coulter counter.

[0058]

Examples 2 – 3 and Comparative Examples 1 – 6

Procedure of Example 1 was followed, except changing the average particle size (μm) and contents (weight parts) of the gel process silica and precipitation process silica in the coating solution, to those shown in Table 1, to prepare inkjet recording papers.

[0059]

Spread of ink dots, writing property, and smoothness/flatness of the thus-prepared inkjet recording papers were evaluated, and results are shown in Table 1.

< Evaluation >

(1) Spread of ink dots : After printing an aqueous ink (black) by using a printer (model BJC-400J, manufactured by Canon K.K.) in standard mode, extent of the spread of ink dots was measured by using an image analyzer (model SPICA II, manufactured by Nipon Avionix K.K.). Following three grades were employed as the standard for evaluation. There is no practical problem if the grade is O.

O : Size of the ink dot is smaller than 0.2 mm
Δ : Size of ink dot is0.2 – 0.3 mm
X : Size of ink dot is larger than 0.3 mm

(2) Writing property : Hand writing was made on an inkjet recording paper, using a pencil (hardness = H). Evaluation of writing property was made based on the following standard.

⊙.....Very easy to write
O..... Easy to write
Δ..... Slightly difficult to write, but is still tolerable
X..... Difficult to write. Have practical problem.

(3) Smoothness/flatness : Smoothness/flatness (in seconds) of the surface of the thus-obtained inkjet recording paper was measured by a Becks' level meter (manufactured by Kumagaya Riki K.K.).

[0060]
[Table 1]

	Gel process silica		Precipitation process silica					
	Av. particle size	Weight parts	Av. Particle size	Weight parts	Difference of particle sizes	Spread of ink dots	Writing property	Smoothness/ flatness
Example 1	8.0	35	6.0	65	2.0	0.14 O	O	40
Example 2	5.0	20	3.0	80	2.0	0.11 O	O	75
Example 3	3.0	50	8.0	50	5.0	0.14 O	◎	30
Example 4	6.0	20	6.0	80	0.0	0.13 O	Δ	45
Comparative Example 1	-	-	6.0	100	-	0.13 O	x	70
Comparative Example 2	8.0	100	-	-	-	0.35 x	◎	13
Comparative Example 3	8.0	5	6.0	95	2.0	0.14 O	x	50
Comparative Example 4	5.0	80	6.0	20	1.0	0.30 Δ	O	60
Comparative Example 5	10.0	20	10.0	80	0.0	0.45 x	*Δ	10

*Δ : It means the level in x - Δ range.

[0061]

Results illustrated in Table 1 gave the following facts. Thus, when gel process silica alone was used (Comparative Example 1), spread of ink dots was excessive. When precipitation process silica alone was used (Comparative Example 2), it gave insufficient writing property. When a mixture of gel process silica and precipitation process silica was used and the contents of both types of silica were beyond the range specified in Claim 1 (Comparative Examples 3 and 4), results were poor. Thus, when the content of gel process silica was deficient (Comparative Example 3), writing property was poor. And, when content of gel process silica was excessive (Comparative Example 4), the ink dots tended to spread more. And, when the average particle size of the precipitation process silica exceeded 8 μm (Comparative Example 5), the ink dots tended to spread slightly more even if both gel process silica and precipitation process silica were used together. On the other hand, when both gel process silica and precipitation process silica were used together and their contents were within the range specified in Claim 1 (Examples 1 – 4), spread of ink dots was small, writing property was good, and smoothness/flatness was in a favorable range. And, when the difference of the average particle sizes of the gel process silica and precipitation process silica was smaller than 1 (Example 4), writing property was slightly inferior. However, when it exceeded 1, writing property was good (Examples 1 – 3). And, particularly when the difference of average particle sizes was 5 which was the largest (Example 3), writing property was excellent.

[0062]
[Effect of invention]

According to this invention, problems of the prior art can be solved. And, according to this invention, it is possible to provide an inkjet recording paper that has a quick ink absorbability, smaller spread of ink dots, and good writing property.